

PATENT SPECIFICATION



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COMPLETE SPECIFICATION

Improvements in or relating to Tanning Compositions and Processes for Tanning

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention (which has been communicated to us by E. I. du Pont de Nemours and Co., of Wilmington, Delaware, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

15 This invention relates to compositions adapted to be dissolved in acid to produce silicic acid solutions suitable for use as tanning baths. The invention is more particularly directed to dry compositions comprising a hydrogen bonding agent and an acid-soluble double silicate of an alkali metal and aluminium, chromium, iron, zinc, titanium or zirconium.

25 Practices for tanning skins with silicic acid have recently been improved by the inclusion of a hydrogen bonding agent in the tannage. These newly-improved baths customarily contain a silicic acid sol, a hydrogen bonding agent, and aluminium sulphate, and tanners find considerable difficulty in accurately proportioning the materials needed at the place of use. Many tanners are poorly equipped and unable accurately to measure out the re- 30 actants and to carry out the procedure of preparing the rather complicated tanning solution. Most tanners prefer a composition which can be dissolved and made up ready for use by workmen comparatively unskilled in the manufacture of chemicals.

40 It is an object of this invention to provide prepared compositions which can be readily dissolved in an acidic medium to produce tanning solutions.

45 Thus, according to the invention there are provided solid tanning compositions, adapted to be dissolved in acid to produce a modified silicic acid sol, comprising a hydrogen bonding agent and an acid-soluble, double silicate of an alkali metal and aluminium, chromium, iron, zinc, titanium or zirconium.

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The double silicates have as one cation lithium, sodium or potassium and as a second cation aluminium, chromium, iron, zinc, titanium or zirconium. Silicates such as sodium calcium aluminium silicate may be used. There may also be used, for instance, naturally occurring silicates, for instance, laumonite, analcite, natrolite and nethelite. There may also be used any of the similar compounds prepared commercially, for instance, by reacting a silicate with an aluminium compound, e.g. as described in U.S. Specifications Nos. 2,244,383 and 1,949,360. Sodium aluminium silicates are also produced by heating kaolin with a sodium hydroxide solution. Other double silicates may be produced by analogous reactions. It is preferred to use a water-insoluble, acid-soluble, precipitated double silicate and particularly a precipitated sodium aluminium silicate which is made at a high pH by processes more particularly described hereinafter, preferably having a mol ratio of $\text{Al}_2\text{O}_3 : \text{SiO}_2$ of 1:2 to 1:5.

55 By a "hydrogen bonding agent" we mean organic compounds which form coordination complexes with silicic acid, and which are at least slightly soluble in water without raising the pH of a silicic acid solution above 7. Hydrogen bonds are formed only between the most electronegative atoms, and accordingly the organic compounds we prefer to use contain at least one of the groups $-\text{O}-$, $-\text{OH}$, and $>\text{NH}$. The compounds should not contain groups which will react with silicic acid in aqueous acidic media to give compounds of the conventional sort when such reaction would interfere with hydrogen bonding, and they should preferably not give precipitates with silicic acid. Suitable hydrogen bonding agents are water-soluble ethers, amides, alcohols, ketones and esters of phosphoric acid. It is preferred that the ethers have an oxygen or nitrogen atom in addition to that in the ether linkage and specifically it is desirable that the ether contain in addition to the ether group a second ether group, a hydroxy group, an amide group,

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or an ester group. In the ethers the two carbon atoms attached to the oxygen atom of the ether linkage should not be attached to each other. Amides for use with silicic acid sols according to the present invention are preferably N-substituted. Alcohols for use as hydrogen bonding agents ought to contain more than two carbon atoms. Alcohols are among the weakest of the hydrogen bonding agents but may

find value in some instances. Ketones are not quite as weak as alcohols and any water-soluble ketones may be used as above discussed. Among the characteristics of these silicic acid-hydrogen bonding agent combinations is a decreased tendency to precipitate gelatine and an increase in the time required for the sol to be converted to the gel.

20 Examples of ethers are:—
 Di-, tri-, tetra-, hexa-, and nonaethylene glycols, made by condensation of ethylene glycol at an elevated temperature and fractionation of the product.
 Dimethyl ethers of di- and tetraethylene glycol.
 25 Butyl ether of diethylene glycol.
 Ethyl ether of diethylene glycol acetate.
 Methyl ether of diethylene glycol acetate.
 Monoethyl ether of diethylene glycol.
 Monoethyl ether of ethylene glycol.
 30 Monomethyl ether of ethylene given.
 N : N¹-Bis(beta-methoxyethyl) adipamide made by reacting adipyl chloride with the methyl ether of monoethanolamine.
 N : N¹-Bis(methoxymethyl) urea.
 Polyethylene glycol adipate made by the condensation of adipic acid and ethylene glycol.
 35 Diethyl ether of diethylene glycol.
 Dioxane.
 Dioxolane.
 Diethyl and dimethyl ethers of ethylene glycol.
 40 Dimethyl ether of ethylene glycol.
 Triethylene glycol dipropionate.
 Glycerol formal.
 Ethylene glycol acetal.
 Sorbitol triacetal.
 45 N : N-Dimethylmethoxyacetamide.
 N-Acetylmorpholine.
 N : N¹-Adipylmorpholine.
 Dimorpholide urea.
 Polyethylene oxide.
 50 The reaction products obtained by passing ethylene oxide into ethylene glycol, monomethyl ether of ethylene glycol, glycerol, or ethanolformamide respectively.

Examples of amides are:—

55 Tetramethylurea.
 Tetraethylurea.
 Urea.
 Thiourea.
 N : N¹-Diethyl-N : N¹-diethanolurea.
 N : N : N¹ : N¹-Tetramethyladipamide.
 60 N : N-Dimethylacetamide.
 N : N : N¹ : N¹-Tetramethylsuccinamide.
 N : N : N¹ : N¹-Tetraethylsuccinamide.
 N : N-Diethylacetamide.
 N : N-Diethylformamide.
 65 N : N-Diethylpropionamide.
 N : N-Dimethylformamide.
 N : N : N¹ : N¹-Tetraethylloxamide.
 N : N-Diethylglycolamide.
 N-Ethyl-N-ethanolformamide.
 70 N-Ethyl-N-ethanolglycolamide.
 N-(2 : 3-Dihydroxypropyl)methoxyacetamide.
 N-Butyl-N-Beta-hydroxyethyllactamide.

N-Ethanoethanesulfonamide.

N-Isobutylacetamide.

N : N¹-Diethanoloxamide.

N : N¹-Diethanolsuccinamide.

5 N-Formylhexamethyleneimine.

Diethylcyanamide.

Acetamide.

Succinamide.

Formamide.

10 Examples of ketones are:—

Acetonylacetone.

Acetone.

Methyl acetoacetate.

Examples of alcohols are:—

15 Diacetone alcohol.

2-Methyl-2:4-pentanediol.

Isopropanol.

Pinacol.

Hexamethylene glycol.

20 Pentaglycol.

Tert-Butyl alcohol.

Tetrahydroxy octane.

1:1:1-Trimethylethane.

Propanediol.

25 Examples of esters of phosphoric acid are:—

Tributyl phosphate.

Triethyl phosphate.

Tri-isopropyl phosphate.

Tri-isoamyl phosphate.

30 Hexyl phosphate.

Tri (butyl ether of diethylene glycol) phosphate.

All the above compounds and their methods of preparation can be found by reference to standard reference works such as those abstracted in "Chemical Abstracts".

35 In general, there should be used an amount of hydrogen bonding agent such that when a tanning solution has been made up from the composition the agent will be equivalent to between 0.1 per cent.

40 and 10 per cent. of the weight of the tanning solution.

The compositions may advantageously include masking agents for the alumina or other metal tanning component, for instance, lactates, acetates, propionates, tartrates, glycollate, citrate, oxalate, adipate, succinate, or glutarates of sodium, potassium, ammonium, or an alkaline earth metal the cation being unimportant provided it does not form an insoluble inorganic salt with tanning bath constituents and provided it does not interfere with the tanning process. Small amounts of these masking agents will of course be used in accordance with the customary practice since too much of the masking agent will too greatly retard tanning. In general, from 5 per cent. to 100 per cent. of the weight of alumina, or other metal 55 as oxide, may be used.

60 The compositions may contain still other modifying agents and there may be

included, for instance, other tanning agents and tanning assistants.

In making up tanning solutions with the compositions of the present invention it is only necessary to dissolve the composition in a dilute acid. Ordinarily

dilute sulphuric acid sufficient to bring the pH to a proper value for tanning will 70 be used. Alternatively there may be em-

ployed such acidic materials as sulphamic acid, hydrochloric acid, nitric acid, thiocyanic acids, acetic acid, lactic acid, and other similar inorganic and organic acids. 75

Acid-reacting salts may similarly be used and there may be employed, for instance, sodium bisulphite, monosodium phosphate, acid tartrates, zinc chloride, titanium sulphate, aluminium sulphate, and chromium sulphate. The amount of acid 80

or acidic material will ordinarily be such as to result in a pH of about 1 to 5, preferably about 2 to 3. It will be under-

stood that while any acidic material may 85 be used to increase the acidity of silicate solutions to produce silica sols, some acidic materials do not themselves have a low enough pH to produce the final acidity

desired, and such materials may be used 90

in combination with a more acidic material.

Acids may be included in compositions of the present invention by mixing the compositions with such dry acids and acidic materials as sulphamic acid and sodium acid sulphate. To minimize the reaction between the solid acid and the double silicate one or both the ingredients can be coated with an inert substance prior to mixing. If the compositions are to be stored any length of time there is unfortunately a tendency to premature reaction.

The concentration of tanning agents made up using compositions of the present invention may be considerably varied, but it will rarely be found desirable to have an SiO_2 content greatly in excess of about 2 per cent.

The tanning compositions of this invention may be used to make up tanning baths for the treatment of any type of skin adapted to be converted into leather or fur. It is to be observed that the term "skin" is used generically to include heavy skins such as cowhide, lighter skins such as goatskin and calfskin, and also skins of fur-bearing animals. It will naturally be necessary to adapt the processes to the type of skin to be treated. For instance, goatskin may be more rapidly tanned than calfskin, but those skilled in the art are well aware of such factors and may readily adapt the compositions of this invention to the specific needs of particular specialized problems.

Skins to be tanned employing compositions of this invention may be prepared in any of the manners customary to the art. They may suitably be unhaired, limed, delimed, and bated and pickled. The skins may if desired be de-pickled. They may also be given a salt liquor treatment to soften them and to put them in a more uniform condition as is the practice in prior art tanning processes.

While skins prepared in any manner may be treated using tanning solutions made up with compositions of this invention, the pH of the skins is important. As will be observed below, the tanning is effected at certain conditions of acidity and the skins may tend to change these conditions. The tanning solution may suitably be controlled to compensate for variance of the pH of the skins from that of the tanning solution. It may sometimes be found advantageous to adapt the processes for preparing the skins so that a skin prepared for tanning is approximately at the pH of the tanning solution.

Too rapid reaction of the tanning agent with the skins in the first stages of the process should be avoided in order to pre-

vent surface hardening of the skin. The amount of hydrogen bonding agent used should, as indicated above, be such as to assist in preventing too rapid a tanning and the initial pH of the solution should not be too high. The initial pH of the solution will ordinarily be from about 2.0 to 3.0. If the initial pH is much above 3.5 the tanning will proceed too rapidly in the initial stages though it will be understood that the pH to be selected in any particular instance will depend upon the specific conditions of the tannage. If too low a pH is used combination of silica with the skin is too slow and, additionally, excessive acidity may deleteriously affect the skin.

After satisfactory penetration has been obtained the pH of the solution is raised by the addition of any suitable alkali. Raising the pH accelerates the tanning action. The pH should at this point be raised to about 3.5 to 4.5. Sodium carbonate or other alkali metal or ammonium hydroxides or carbonates or organic bases such as ethanolamines may be used to raise the pH.

The considerations as to the type of apparatus to use, the time to be allowed for tanning, the temperatures of tanning, and the amounts of tanning agent are substantially those known to the art in connection with prior art tanning processes. The time allowed for tanning must be sufficient to permit complete penetration of the tanning agent, and the pH should not be raised too rapidly or there may be puckering and apparent over-tannage of the grain surface. The tanning can best be effected at room temperature, say 20° to 30°C. The exact amount of the tanning solution to use can best be determined by a few simple tests under the specific conditions of the process selected and with the specific skin to be treated. In general, enough of the tanning agent must be used to effect the tanning desired but unduly large amounts should not be used as they will not be taken up by the leather in a reasonable period of time and they may cause over-tannage.

While compositions of the invention may be made as described with various natural and manufactured double silicates, it is preferred to use a precipitated sodium aluminium silicate, or other double silicate, the manufacture of which is hereinafter described.

In the preparation of the precipitated silicates it will ordinarily be found desirable to use a sodium silicate but potassium or lithium silicates may also be used. The $\text{SiO}_2/\text{Na}_2\text{O}$ ratio ought not to be substantially greater than 2. It is preferred

to use sodium metasilicate but if a silicate with a higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratio is used an alkali, for example, sodium hydroxide, potassium hydroxide, calcium oxide, barium oxide or an organic base such as tetraethanolammonium hydroxide will need to be added. In any event the total alkali in the reaction should be sufficient to maintain a pH of 9 or more.

10 Any aluminium compound may be used which is more soluble than the product of reaction with the silicate, for instance, aluminium sulphate, aluminium hydroxide, sodium aluminate, aluminium nitrate or aluminium chloride. When a compound such as sodium aluminate is used it will of course be easier to maintain a pH of 9 or more during the reaction.

15 It will be found a comparatively simple matter to adjust the composition of the precipitated sodium aluminium silicate since almost all, say over 90 per cent., of the silica and alumina used in the reaction will be found in the product. The proportions of reactants should be so selected that the $\text{Al}_2\text{O}_3:\text{SiO}_2$ molar ratio is within the limits from about 1:2 to 1:5, preferably from about 1:3 to 1:4.

20 The alkalinity of the product should be kept down, and the product should generally contain between 1 and 1.5 mols of Na_2O per mol of Al_2O_3 . The use of large excesses of alkali in the reaction should therefore be avoided and the product should be carefully washed.

25 To effect reaction the soluble silicate and the soluble aluminium compound are each first put in solution and then these solutions are brought together. The solution of silicate may ordinarily contain from about 5 to 15 per cent. of solids and the solution of the aluminium compound may similarly contain about 5 to 15 per cent. solids. The final mixture should 30 not contain much in excess of about 20 to 25 per cent. solids by weight. It is desirable to add the aluminium compound 35 solution to the silicate solution. In this way, the presence of local concentrations

40 of aluminium compound having a pH below 9 is most easily avoided. It will be found possible, however, to run the two solutions simultaneously into a mixer in proper ratio, and in general any method 45 of mixing may be effected so long as low pH is avoided. A pH substantially below 9 should not be permitted for a substantial period of time during the reaction, although it may be reduced towards the 50 end of the reaction period to as low as 7 or 8 without markedly injuring the product. It may frequently be found desirable after the reaction is substantially concluded, therefore, to reduce the pH so 55 that the product will be substantially

neutral. After the reaction is concluded the precipitate may be filtered and washed.

Other double silicates using any alkali metal and aluminium, chromium, iron, zinc, titanium or zirconium may be prepared in a similar manner.

The following Examples are illustrative of the preparation of acid-soluble double silicates adapted for use in the compositions of this invention:—

EXAMPLE I.

A precipitated sodium aluminium silicate was prepared as follows:—

24.9 parts of commercial iron-free aluminium sulphate (containing 16 per cent. Al_2O_3) dissolved in 132 parts of water were slowly added with vigorous agitation to a solution containing 31.5 parts of a sodium silicate solution containing $\text{Na}_2\text{O}=9.1\%$ and $\text{SiO}_2=29.7\%$ and 10.0 parts of flake caustic soda (equivalent to 6.85 parts of Na_2O) dissolved in 175 parts of water. The $\text{SiO}_2:\text{Na}_2\text{O}$ ratio by weight of the final silicate solution used was 0.96. The additional sodium hydroxide was used to maintain a pH of about 9 during the reaction. The aluminium sulphate was added directly into the vortex of a stirrer so as to have rapid and efficient mixing, and after all the aluminium sulphate had been added, the reaction slurry was stirred for 15 minutes to insure complete reaction. The product was filtered out, washed to remove the sodium sulphate and then dried for 15 hours at 110—115°C. 18.0 parts by weight of the dry product was obtained containing 43.20% SiO_2 , 22.41% Al_2O_3 , 17.24% Na_2O and 17.70% ignition loss. The yield was 97.2% of the theoretical. This particular product had a ratio of SiO_2 to Al_2O_3 of 3.28 to 1, and a ratio of Na_2O to Al_2O_3 of 1.26:1. The product was amorphous, soft, chalky, white, and opaque and it was found well adapted for use in tanning compositions of the invention.

EXAMPLE II.

44.0 parts by weight of commercial iron-free aluminium sulphate (16.0 per cent. Al_2O_3), dissolved in 180 parts of water, were reacted with 83.16 parts of sodium metasilicate (28.62 per cent. SiO_2) dissolved in 400 parts of water. The solutions were mixed as outlined in Example I. At no time during the reaction did the pH go substantially below about 9. The precipitate was filtered out, washed and dried. The material thus obtained was white, chalky, amorphous, easily pulverized, and very soluble in dilute acids. Analysis showed it to contain 19.03% Al_2O_3 , 15.45% Na_2O , 48.90% SiO_2 and 15.25% loss on ignition. $\text{SiO}_2:\text{Al}_2\text{O}_3=130$

4.35:1 and $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3 = 1.33:1$ in the final product.

EXAMPLE III.

The acid-soluble, precipitated sodium aluminium silicate can also be prepared by using procedures similar to those of the previous examples but by reacting a solution of sodium aluminate with a solution of sodium metasilicate. The products produced were white, porous, and easily pulverized. When the reactants had an $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 4:1 the product had a ratio of 2.78:1. When the reactants had a ratio of 6:1 the product had a ratio of 3.01:1. Similar products were made containing smaller amounts of SiO_2 but these were less readily soluble. The products had $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ ratios of about 1.0 to 1.4.

EXAMPLE IV.

16.25 parts of commercial iron-free aluminium sulphate (16.0 per cent Al_2O_3) were dissolved in 80.0 parts by weight of water. Concentrated caustic solution was added to this solution until the precipitate which first formed redissolved. This solution was then added with violent agitation to a solution containing 10.48 parts by weight of sodium metasilicate in 75 parts by weight of water. The $\text{SiO}_2:\text{Al}_2\text{O}_3$ was 2:1 in this reaction mixture. The pH throughout the reaction was maintained about 11. The precipitate which formed was filtered, washed and dried. A white, porous, easily pulverized material was obtained. This material was rather difficultly soluble in acid solution. Analysis showed it to contain 38.85% SiO_2 , 29.78% Al_2O_3 , 18.29% Na_2O , and 12.68% loss on ignition. SiO_2 to Al_2O_3 ratio in the product = 2.21 to 1, and Na_2O to $\text{Al}_2\text{O}_3 = 1.0$ to 1.

EXAMPLE V.

20.5 parts of sodium aluminate ($\text{Na}_2\text{Al}_2\text{O}_4$) dissolved in 240 parts of water were added with stirring to a solution containing 101 parts of a sodium silicate solution ($\text{Na}_2\text{O} = 9.1$ per cent, $\text{SiO}_2 = 29.7$ per cent) and 22.2 parts of sodium hydroxide dissolved in 1120 parts of water. As in the previous examples, a white, flocculent precipitate formed and was filtered out, washed and dried. The pH during the reaction did not fall below about 11. The product was identical in appearance to those described in the previous examples and was easily acid soluble.

The following Examples, in which the parts are by weight, are illustrative of tanning compositions of the invention:—

EXAMPLE VI.

A tanning composition was made up by mixing together 27.5 parts of the precipitated aluminium silicate prepared as in Example I and 11.2 parts of urea.

For tanning, 35.5 parts of sulphamic acid was dissolved in 200 parts of water and the prepared composition dissolved therein. 100 parts of drained goatskin which had been prepared in the usual way by unhairing, deliming, and pickling were put into this solution in a tanning drum and thoroughly mixed. The skins were agitated for one hour and then the addition of a 10% solution of sodium acetate was begun. By repeated additions of sodium acetate over a course of 7.5 hours, the pH of the solution was brought to a final value of pH 4.0. The solution was then drained from the drum. The tanned skins were piled down over night. The next morning they were brought to a pH of 5.5 with 10% sodium bicarbonate solution during 1½ hours with further agitation. Subsequently the hides were washed with water and fatliquored with a sulphonated oil-Neatsfoot oil mixture. The tanned skins were very soft, pliable, white, and had a shrink temperature of about 185 to 190° F.

A similar composition was made up in which the dry sulphamic acid was admixed with the precipitated aluminium silicate and urea. This mixture was fairly stable and for use it needed only to be added to a correct amount of water.

EXAMPLE VII.

50 parts of pulverized precipitated sodium aluminium silicate prepared according to Example I were intimately mixed with 5.8 parts of nonaethylene glycol. The latter is a liquid material, but due to the extreme porosity and absorbent nature of the precipitated sodium aluminium silicate, the liquid nonaethylene glycol is completely absorbed, the mixture appearing to be a dry powder.

The tanning composition thus prepared can be dissolved in an acid solution for use in tanning as in Example VI.

EXAMPLE VIII.

50 parts of precipitated sodium aluminium silicate were mixed with 21.8 parts of tributyl phosphate. As in the previous example, although the tributyl phosphate is a liquid, the resulting mixture is an apparently dry light powder. The tanning composition may be used as in Example VI by dissolving it in a dilute acid.

EXAMPLE IX.

50 parts of sodium aluminium silicate prepared as in Example I were mixed with 25 parts of powdered urea, and 25 parts of sodium acetate which had previously been pulverized to pass a 100 mesh screen. The mixture was agitated until the ingredients were thoroughly intermingled.

Upon dissolving this composition in dilute sulphuric acid a tanning solution is 130

produced containing silicic acid, a hydrogen bonding agent, aluminium sulphate and a masking agent.

EXAMPLE X.

5 101.5 parts of granular sodium acid sulphate in the form of shot of such a size that it will pass through a 6 mesh screen but not through a 30 mesh screen were mixed with 41.1 parts of sodium 10 aluminium silicate and 17.7 parts of tributyl phosphate.

When this mixture is added to about 800 parts of water and thoroughly stirred for 15 minutes, there is obtained a solution 15 of silicic acid having tributyl phosphate emulsified in it. This solution functions admirably in tanning hides according to the procedure previously described. A composition as shown in this example is 20 none too stable and it should be used within a fairly short time.

EXAMPLE XI.

103 parts of sodium acid sulphate of the type used in the previous example 25 were mixed with 41.1 parts of precipitated sodium aluminium silicate, 20.0 parts of urea and 33.0 parts of anhydrous sodium acetate.

When this mechanical mixture is dissolved in about 800 parts of water, a solution 30 is obtained suitable for tanning.

In order to prevent segregation of the various ingredients from these mechanical mixtures, it is advantageous to mix them 35 thoroughly and then compress the mixture into pellets or small briquettes which readily disintegrate upon being agitated with water.

Although the particle size of the ingredients 40 is not important if the mixture is to be used within a few days, it will be found that if all the ingredients are finely pulverized prior to mixing, some interaction between the sodium acid sulphate 45 and the sodium aluminium silicate will take place. In order to minimize this effect, it is preferred to use relatively coarse sodium acid sulphate in the shotted form, since in this state it is much less reactive than when pulverized to 100 mesh.

In order to minimize the reaction between the solid acid and the sodium aluminium silicate, one or both ingredients 55 can be coated with an inert substance prior to mixing, e.g., the sodium bisulphate pellets may be stirred with 2% of calcium stearate which coats the pellets with a thin white adherent film, before 60 mixing with the sodium aluminium silicate.

EXAMPLE XII.

Fifty parts of laumonite, a naturally occurring calcium sodium aluminium silicate, were ground to pass a screen having 65

300 meshes to the linear inch and mixed with 20 parts of powdered urea which had been previously pulverized to pass the 100 mesh screen. The mixing was continued until the ingredients were thoroughly 70 intermingled.

The tanning composition may be used as in Example VI, by dissolving it in dilute sulphamic acid solution, using sufficient acid to maintain the mixture at a 75 pH of about 2 until substantially all the acid-soluble material in the mineral is dissolved. Tanning with this solution may then be carried out as in Example VI.

EXAMPLE XIII.

50 parts of sodium aluminium silicate of the gel-type similar to that described in the U.S. Specification No. 2,244,383 were ground so as to pass a screen showing 300 meshes to the linear inch and 85 thoroughly mixed with 11.6 parts of carbital acetate.

This tanning composition may be dissolved in sufficient dilute acid solution so that the pH is maintained at around 2 90 until all the mixture is dissolved. The gel-like sodium aluminium silicate dissolves at a much slower rate than the precipitated material. The tanning procedure is carried out as described in Example 95 VI.

Tanning compositions similar to those of the example may be made up using hydrogen bonding agents and double silicates of chromium, iron, zinc, titanium or 100 zirconium.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim 105 is:

1. Solid tanning compositions adapted to be dissolved in acid to produce a modified silicic acid sol, comprising a hydrogen bonding agent and an acid-soluble double silicate of an alkali metal and aluminium, 110 chromium, iron, zinc, titanium or zirconium.

2. Solid tanning compositions as claimed in Claim 1 in which the acid-soluble double silicate is a sodium aluminium silicate.

3. Solid compositions, as claimed in Claim 1 in which the acid-soluble double silicate is a precipitated sodium aluminium silicate having an $\text{Al}_2\text{O}_3:\text{SiO}_2$ molar ratio between 1:2 and 1:5 and an $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio between 1.0 and 1.5.

4. Solid tanning compositions as 125 claimed in any of the preceding claims in which the hydrogen bonding agent is a water-soluble ether, amide, alcohol, ketone or an ester of phosphoric acid.

5. Solid tanning compositions as 130

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claimed in any of the preceding claims in which a masking agent is included with the ingredients.

6. Solid tanning compositions as hereinbefore particularly described and ascertained.

7. A process for tanning skins wherein there are used the compositions claimed in Claims 1—6 dissolved in a dilute acid.

8. A process for tanning skins as hereinbefore particularly described and ascertained.

9. Skins whenever tanned by the process claimed in claims 7 and 8.

Dated the 2nd day of April, 1943.

E. A. BINGEN,
Solicitor for the Applicants.

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